INTERNATIONAL SOLDIER SYSTEMS CONFERENCE AND EXHIBITION 2004

# ADVANCES in MEMBRANE-BASED CHEMICAL/BIOLOGICAL PROTECTIVE CLOTHING for FUTURE SOLDIER SYSTEMS

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**Individual Protection Directorate**

**The Science Behind the Warrior:**

**Yesterday, Today and**

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# Outline

## Part I – Ion Implanted Membranes

## Part II – Membranes Modified with Novel, Surface Bilayers

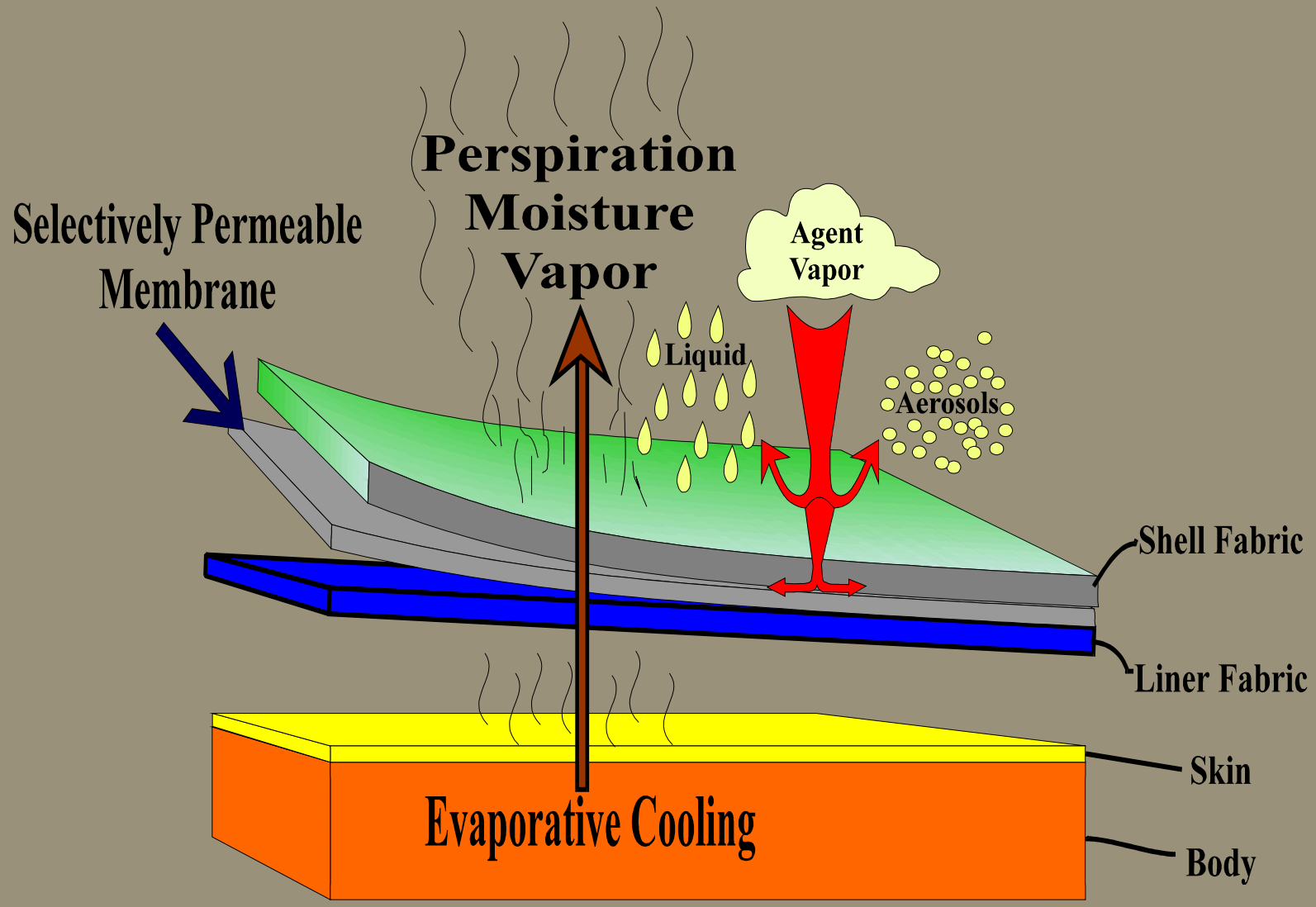
# Purpose

- Improve the permselectivity of membrane materials for use in chemical/biological (CB) protective clothing through the ion beam modification of the surface layers of available membranes
- Two-fold approach: computer modeling of the irradiation process to develop a better understanding of the process at the molecular level and irradiation experiments of materials at different energy levels and with different ions for permselectivity measurements.
- Correlation between the two efforts will ultimately yield a powerful tool for the development of permselective membranes for CB protective garments.

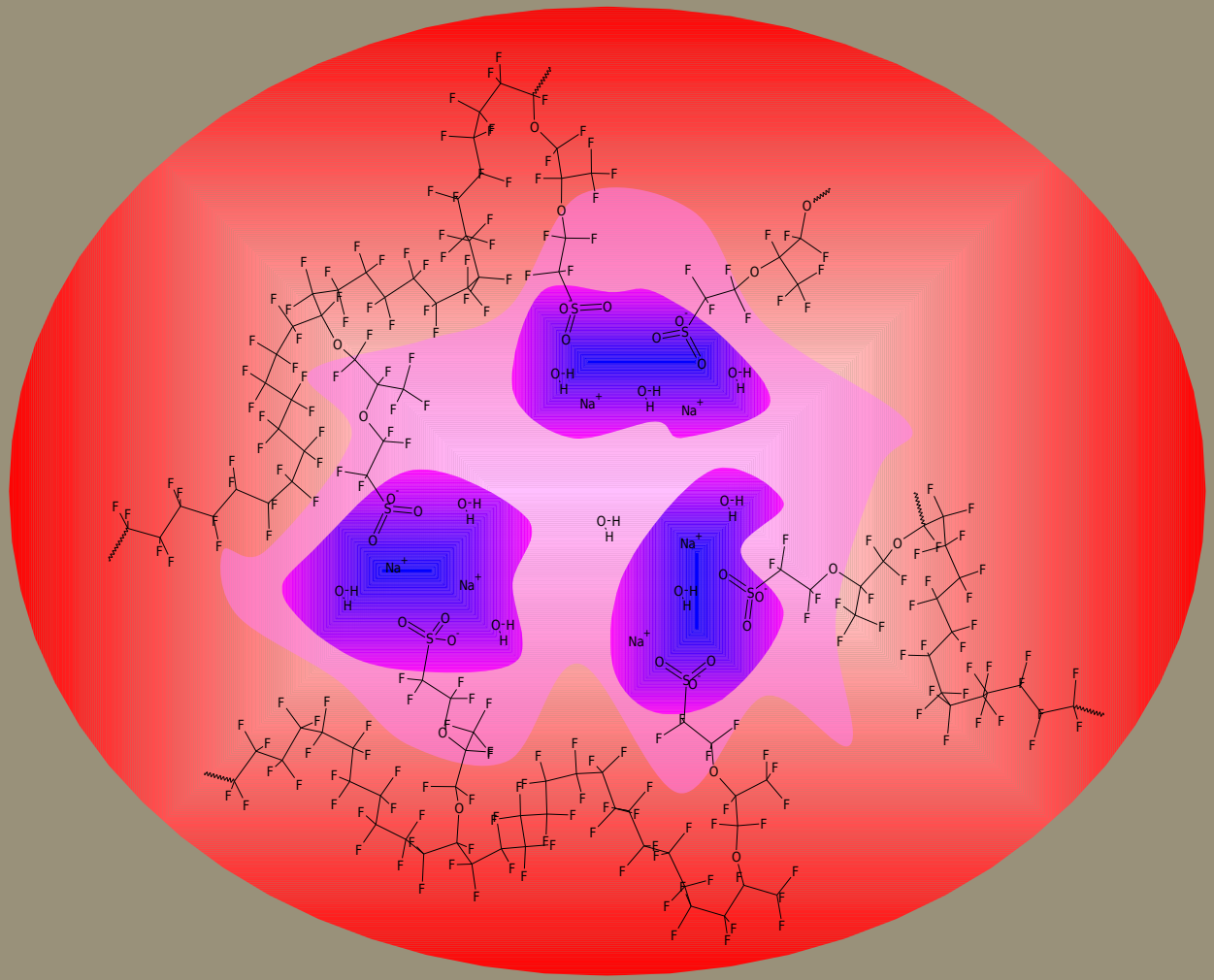
# Introduction

- **Drawbacks to fielded clothing systems:**
  - Heavy, bulky, cumbersome, subject the wearer to heat stress during high metabolic activity
  - Based on activated carbon included in textile system
  - Air-impermeable elastomers for gloves and overboots
- **The ideal permselective membrane for CB protective garments would provide a high moisture vapor transport rate, high enough for sufficient evaporative cooling even during high metabolic rates, while serving as a barrier to CB agents.**
- **Ion beam irradiation is well-suited for the controlled modification of the gas-solid interface, crucial in determining permeation behavior.**

# Material Concept

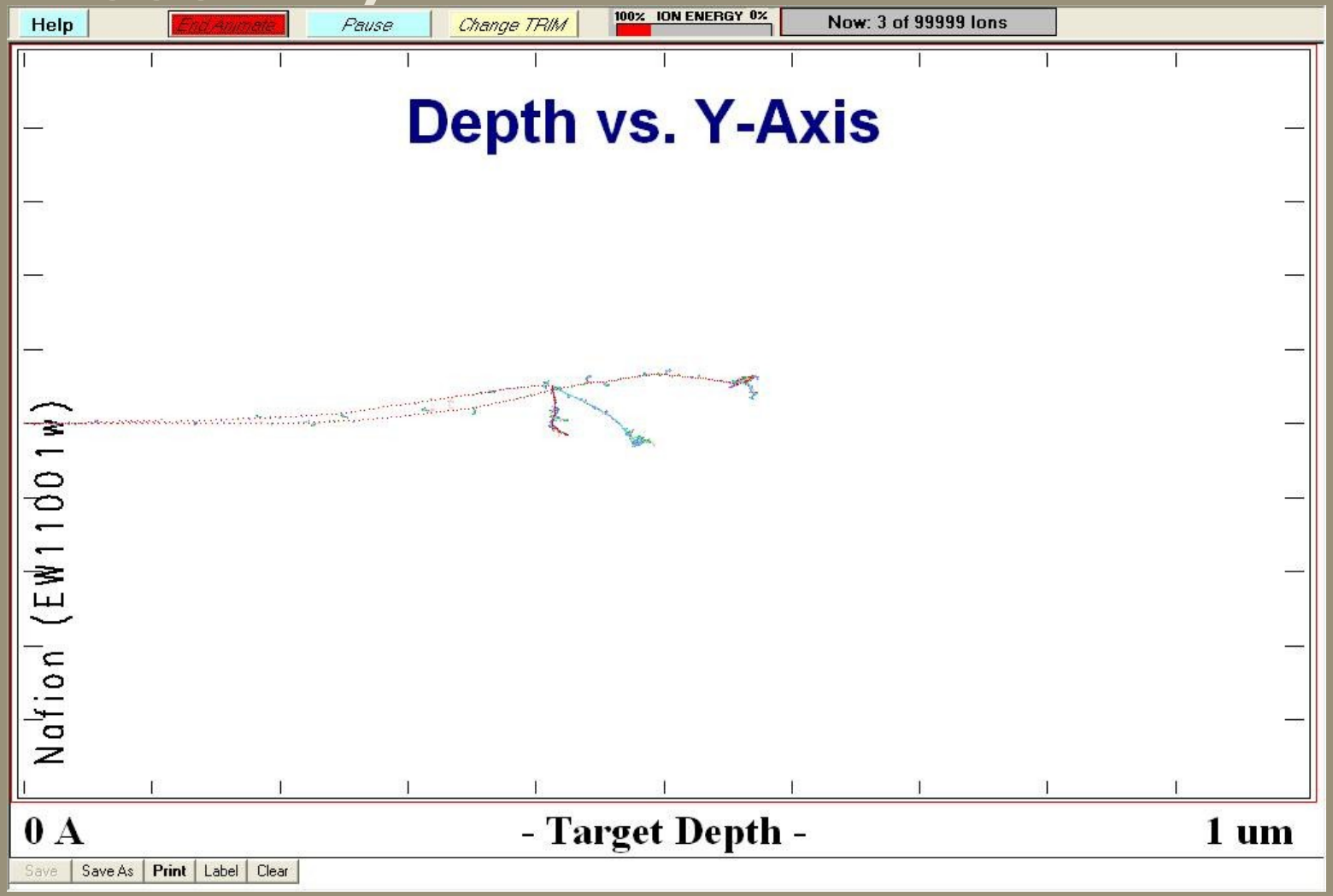


# Nafion® (du Pont): $[—(CF_2CF_2)_n\text{-}(CF_2CF(OCF_2CF(CF_3)OCF_2CF_2SO_3H))—]$

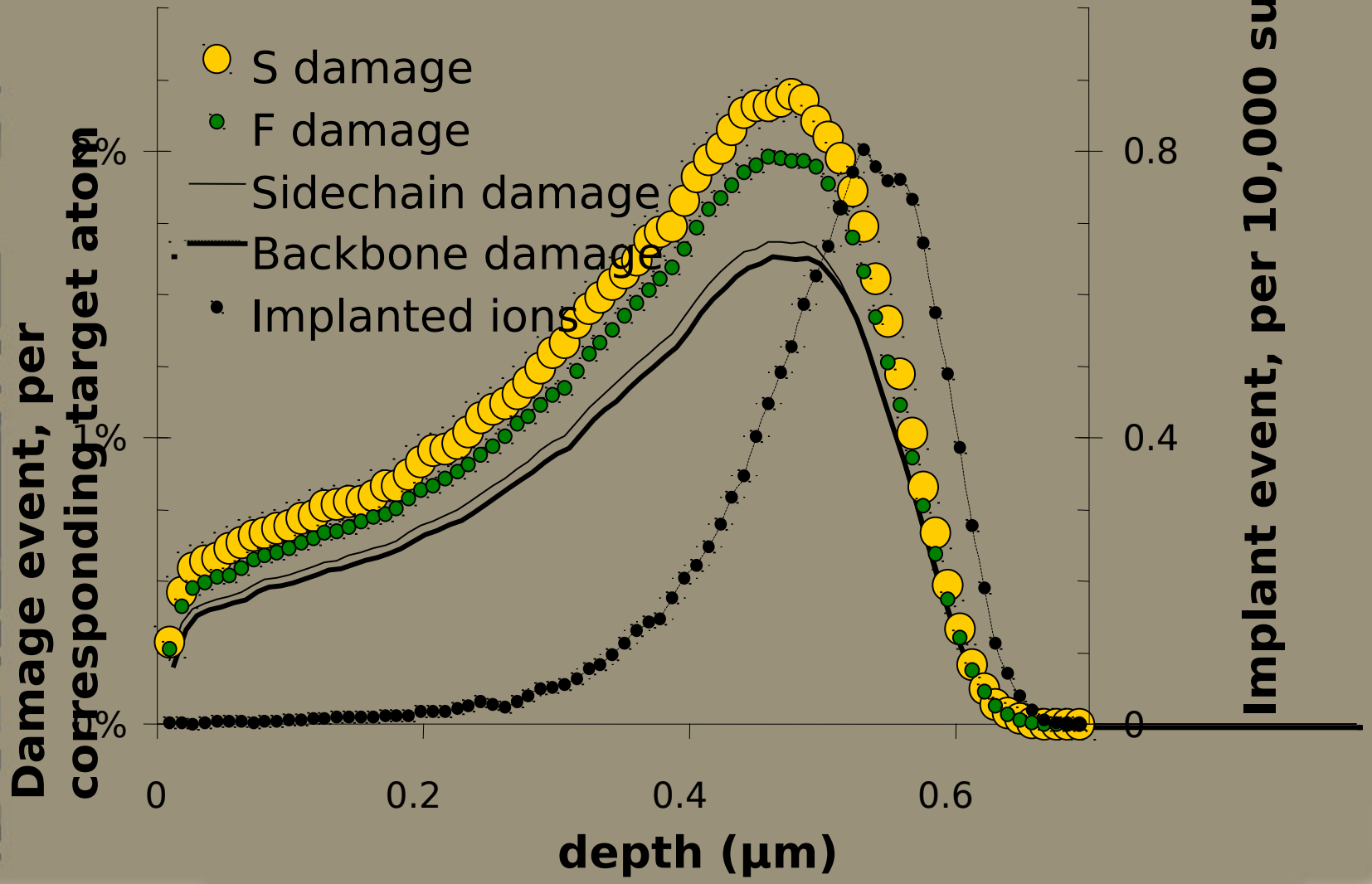


Schematic model of Nafion:
hydrophilic, intermediate and hydrophobic phases

# Transport of Ions in Matter (SRIM v.2000.41 )[1]

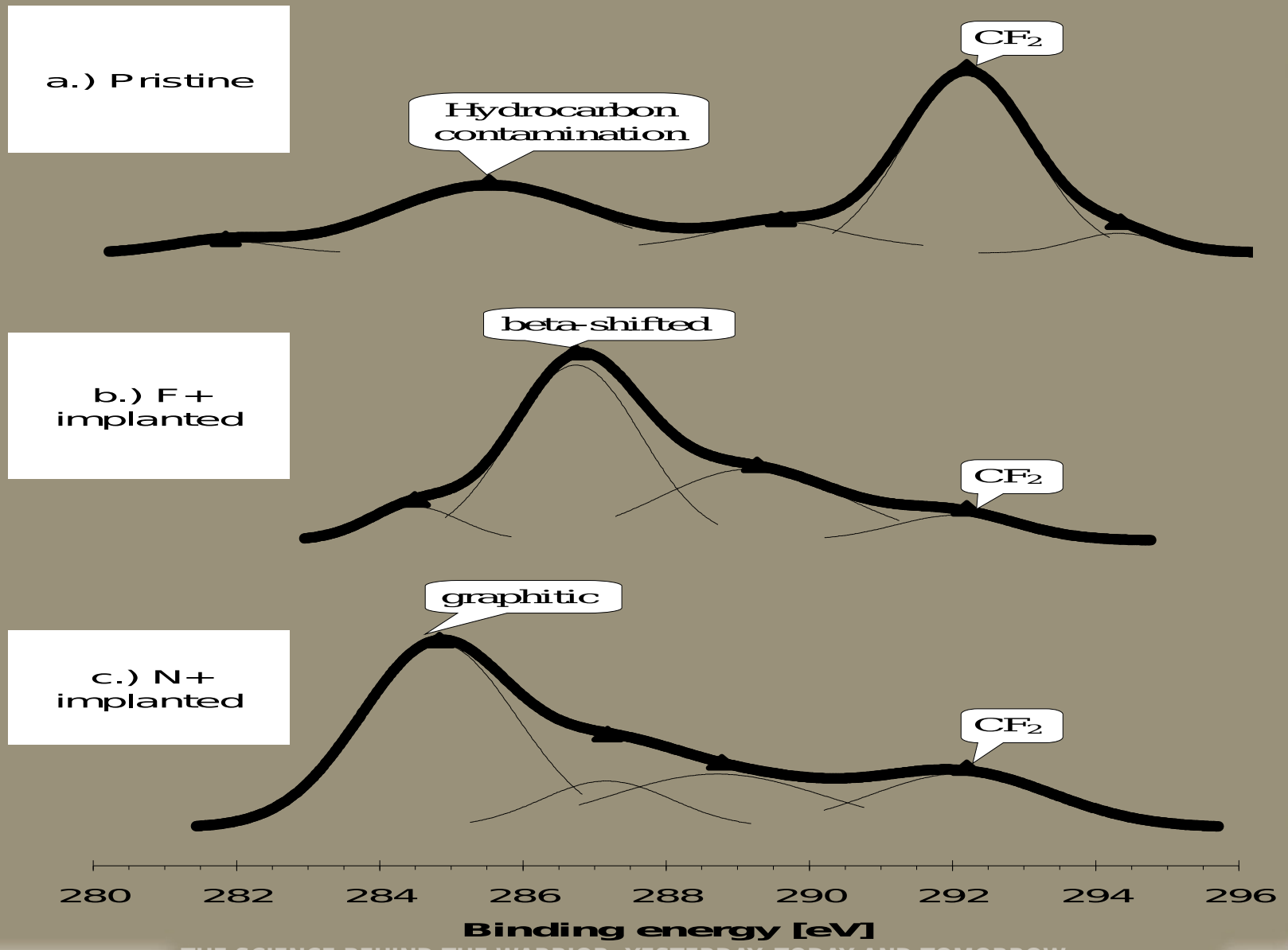


# Example of simulation profile



# Surface analysis:

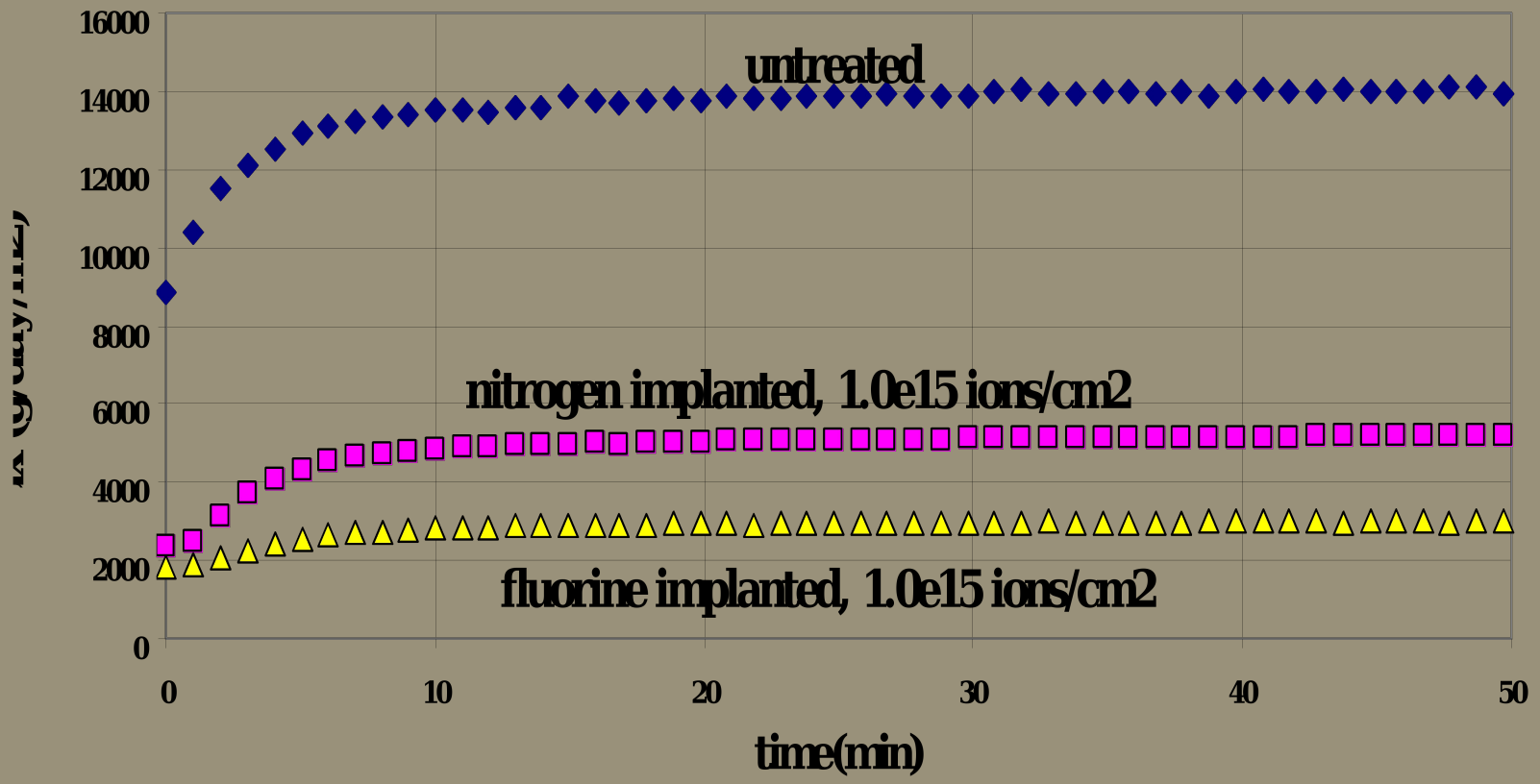
## $C_{1s}$ XPS spectra of pristine and ion beam damaged Nafion®



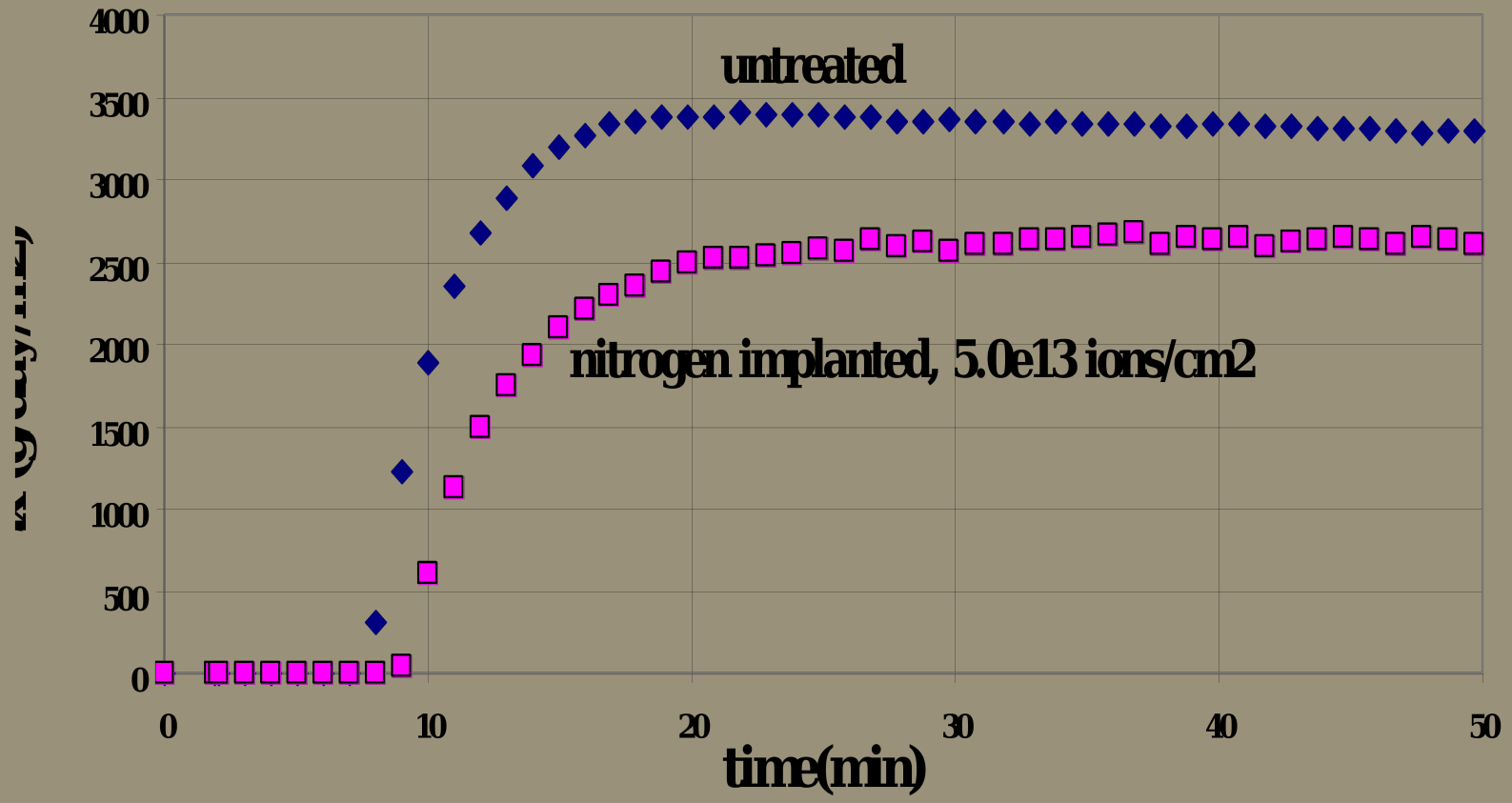
# Interpretation of surface analysis by XPS

- X-Ray Photoelectron Spectroscopy (XPS) provides information on the near-surface layer (down to ca. 50 Å).
- Large changes upon ion implantation are observed,
  due to drastic bond-breaking in Nafion®
- Loss of fluorine is seen in the quantitative elemental analysis
- Ion bombardment ultimately leads to the formation
  of a carbonized layer

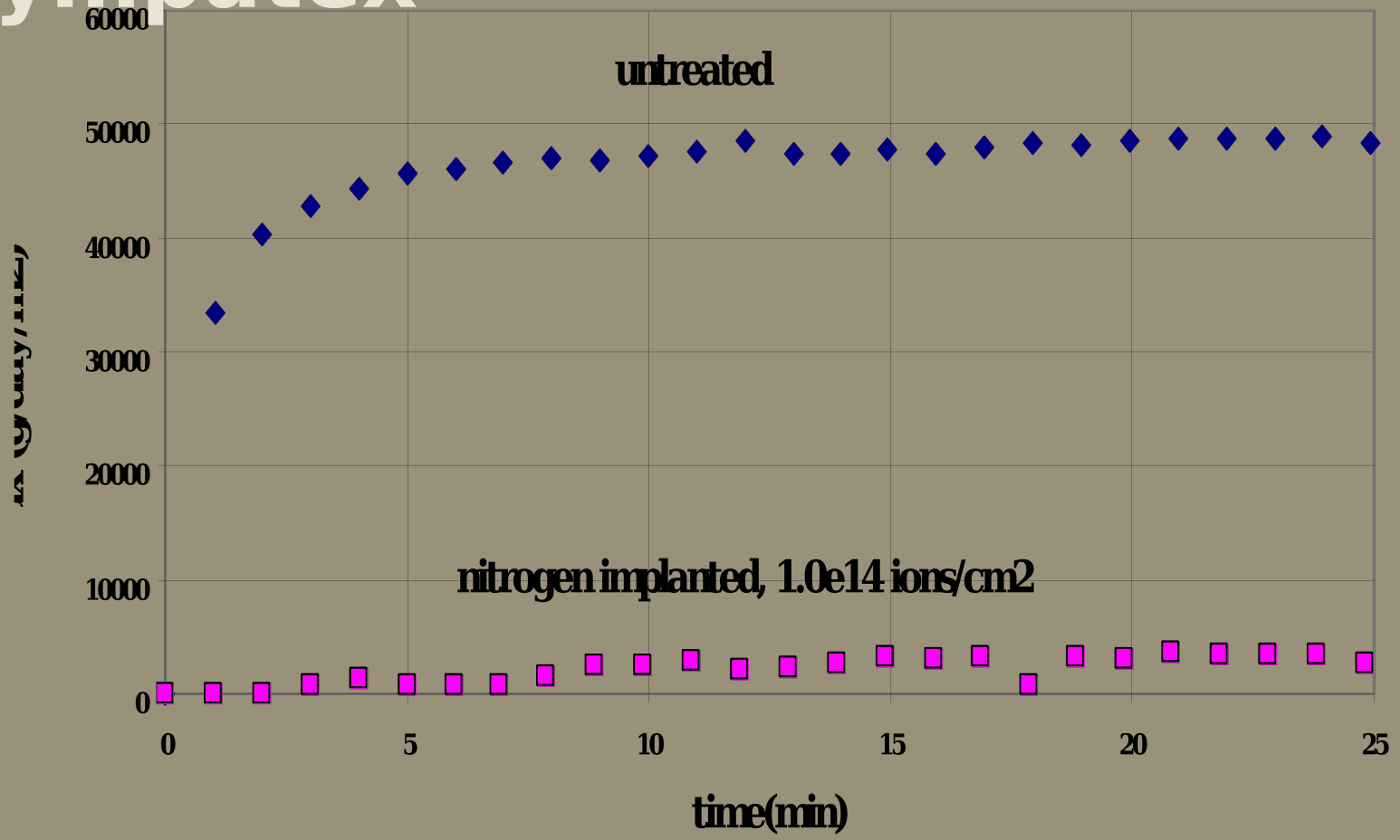
# Water Permeation in NAFION 117



# N-propanol Permeation in NAFION 117



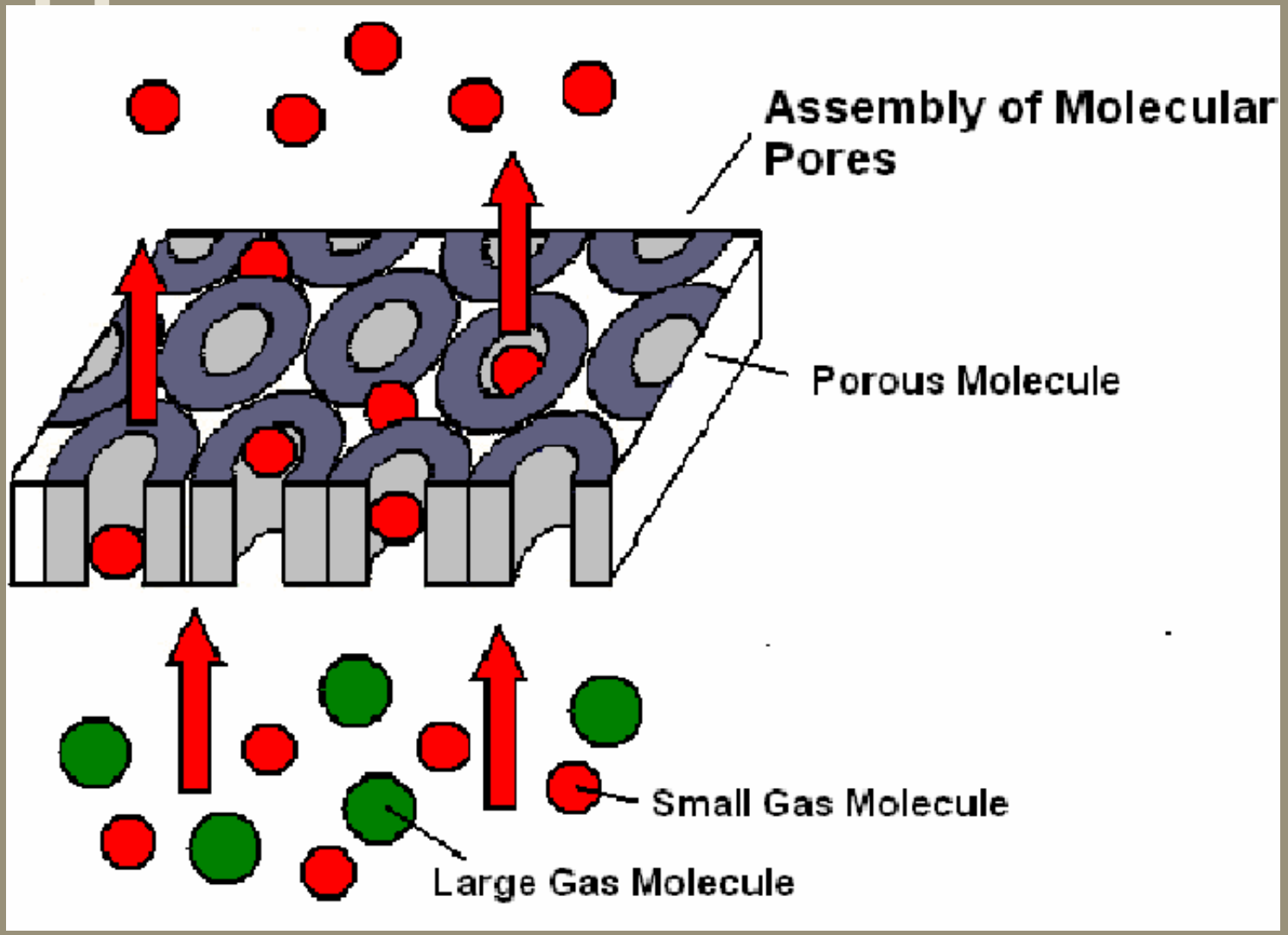
# TCE Permeation in Akzo Sympatex



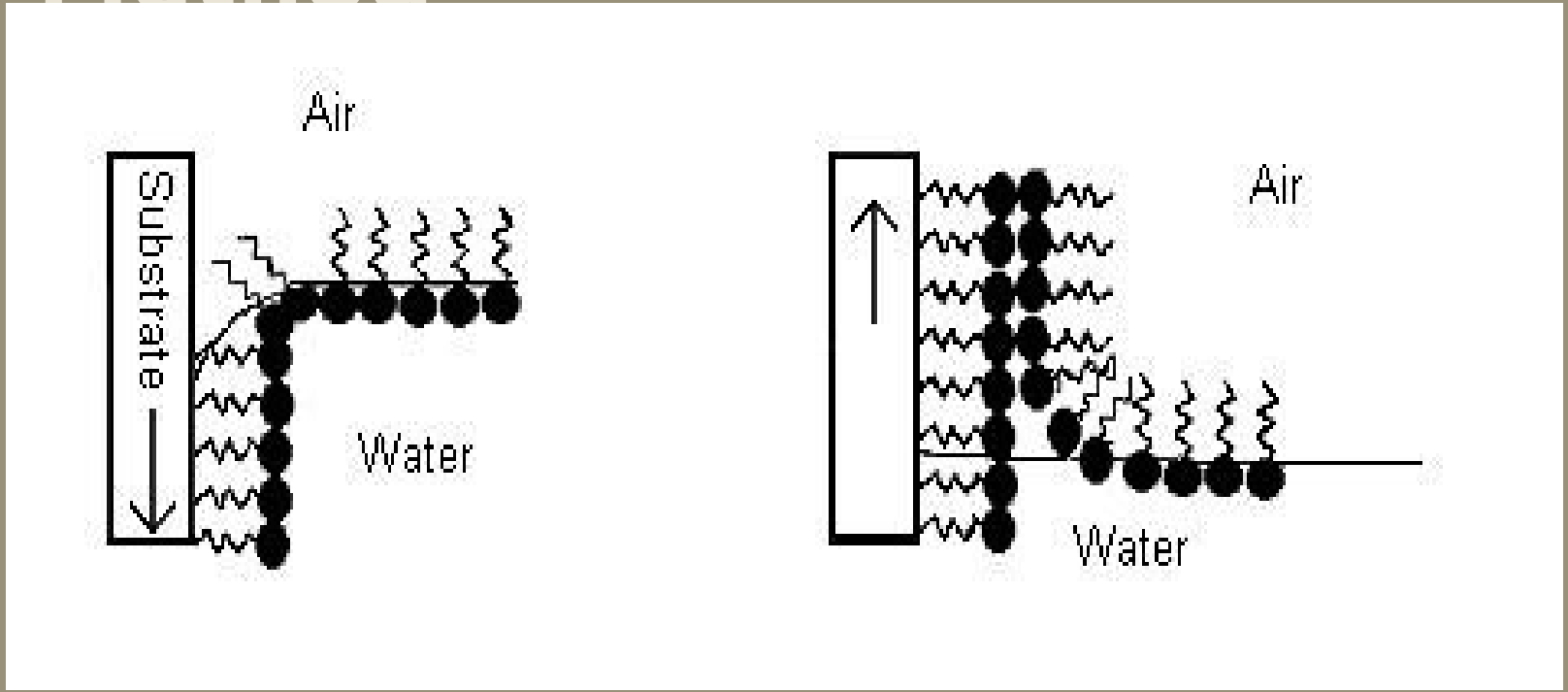
# Summary

- Medium-energy ion beam treatment is a promising technique for developing barrier membranes selectively permeable to water vapor.
- Theoretical calculations are a useful adjunct for optimizing treatment conditions.
- XPS measurements of the surface reveal that ion bombardment leads to loss of fluorine, with the eventual formation of a carbonized layer.
- This two-pronged approach will ultimately yield a powerful technique for the development of permselective membranes for CB protective garments.

# Perforated Monolayer Approach

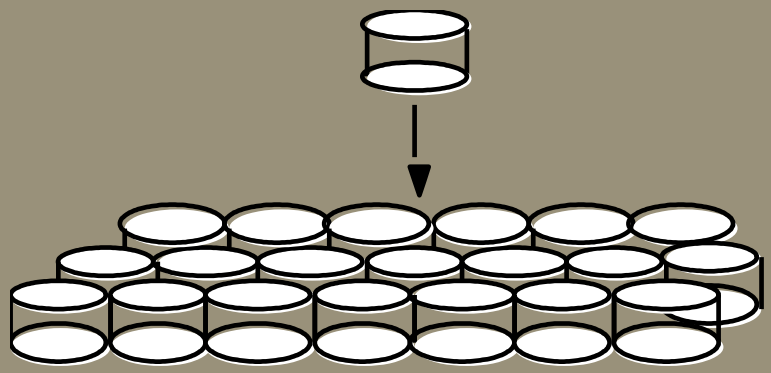


# The Langmuir-Blodgett Method



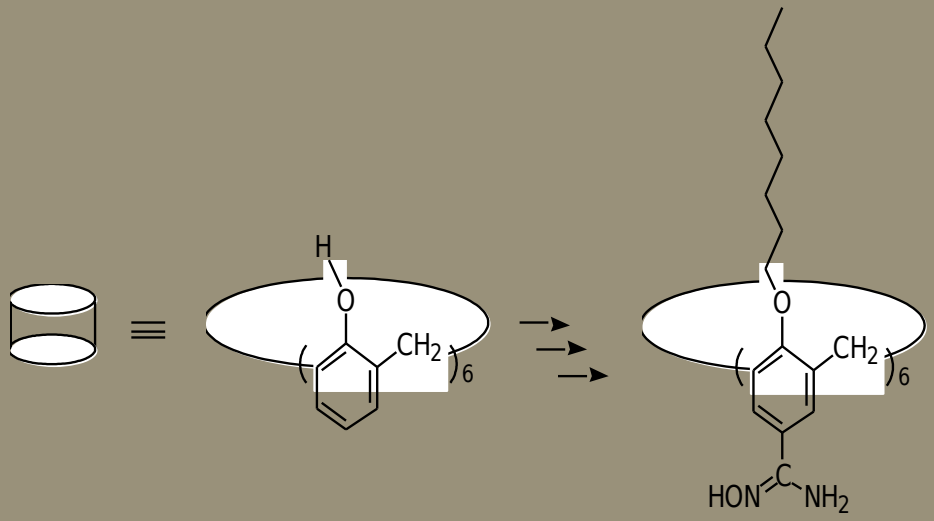

A stylized illustration showing a single surfactant monolayer being transferred to a hydrophobic supp on a down-trip, followed by the transfer of a second monolayer on the up-trip, to form a bilayer.

# Perforated Monolayers



porous surfactant

perforated monola

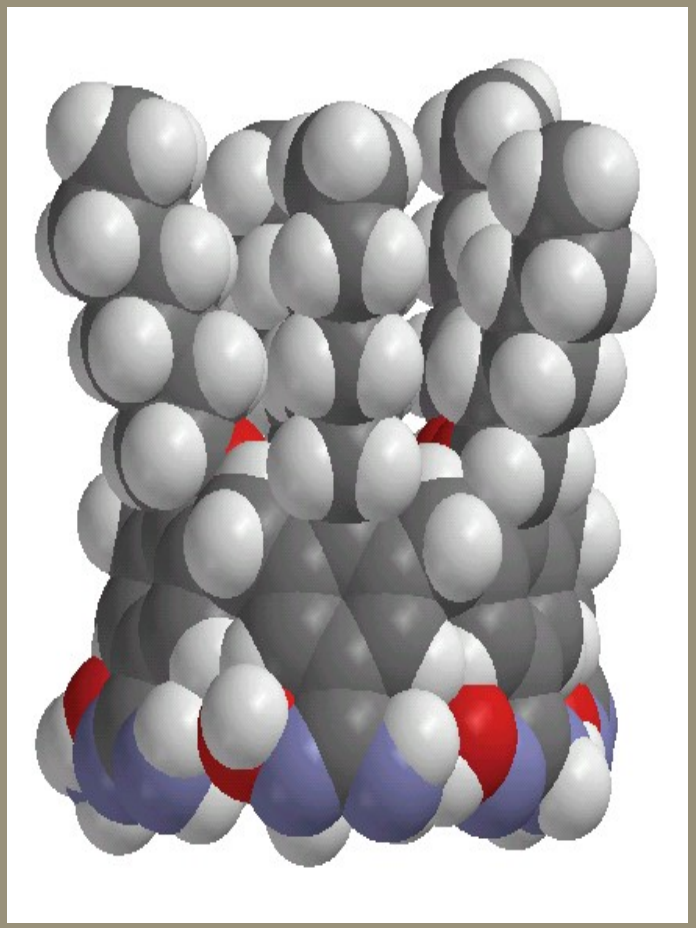



calix[6]arene

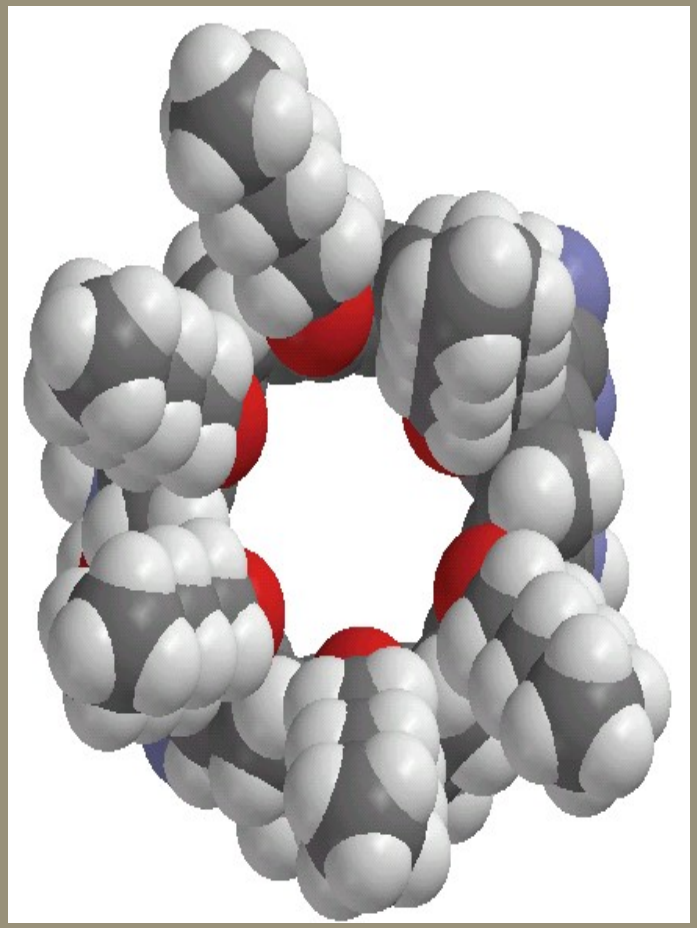
II

An illustration of a perforated monolayer formed from a porous surfactant

# Space filling models of an analog of II

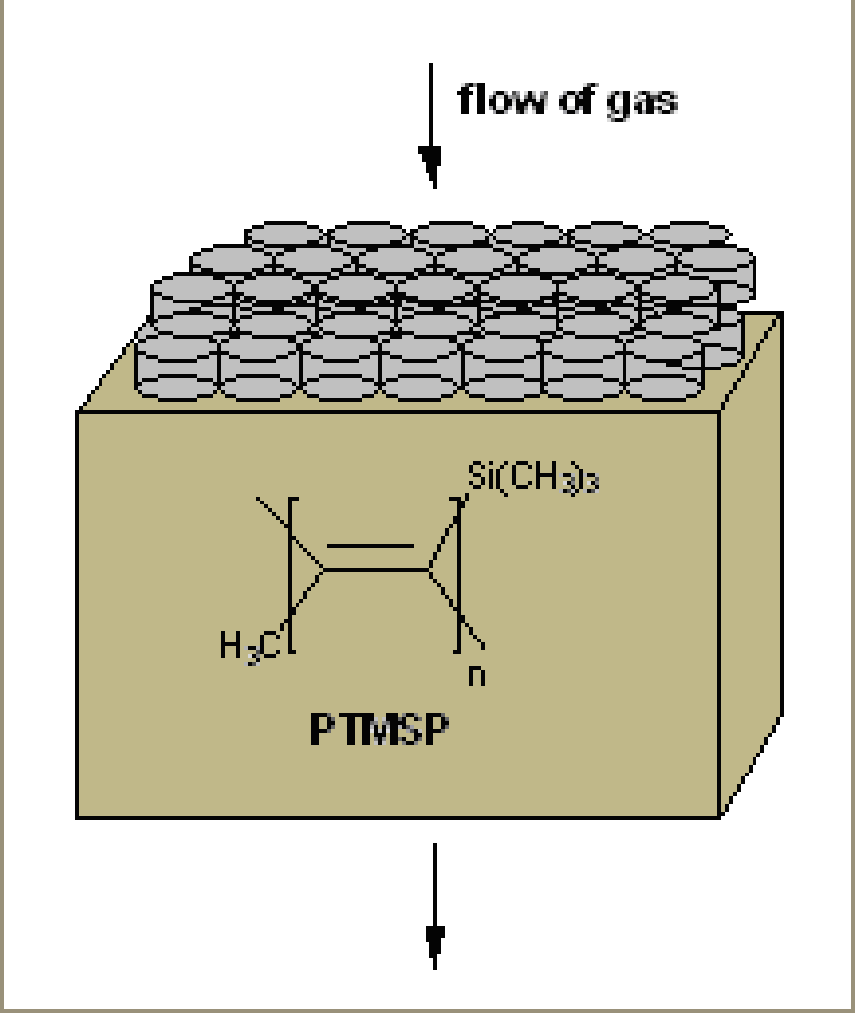


Side View

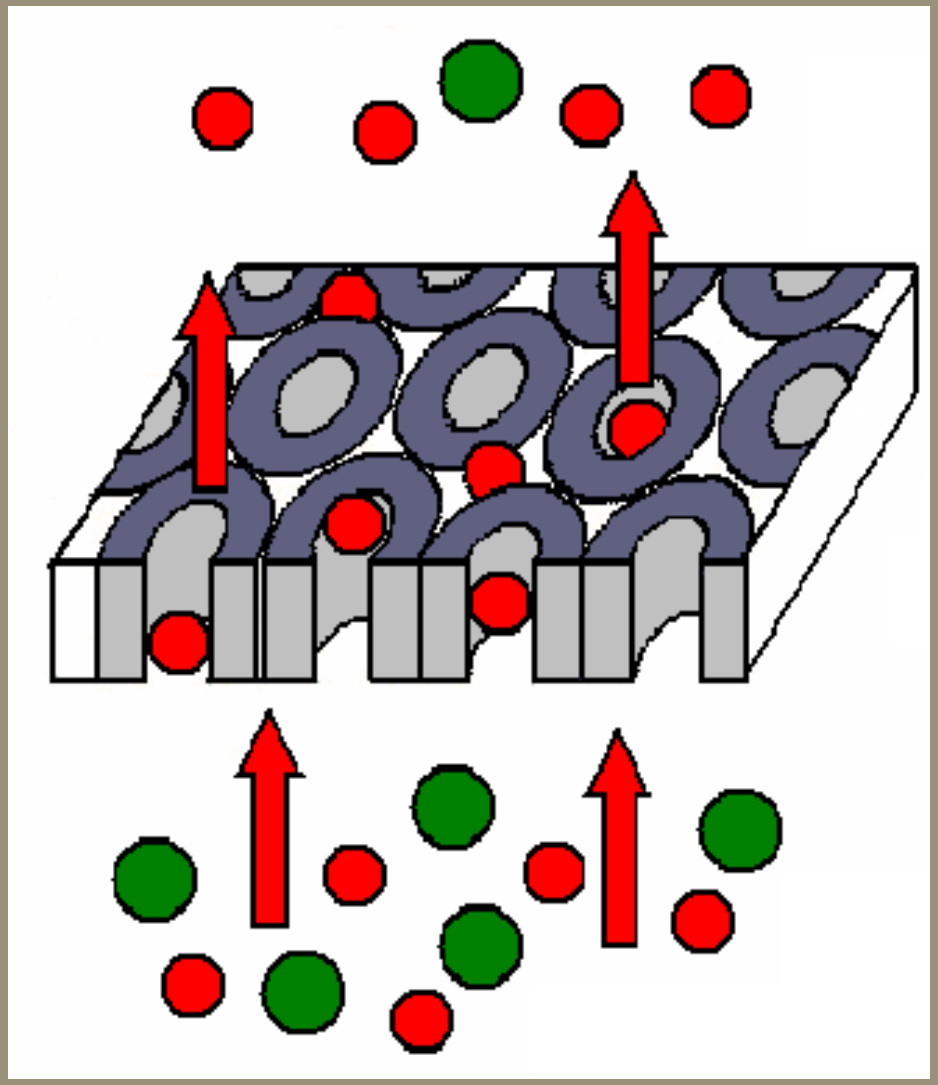


Top View

# Composite membrane formed from a bilayer of ll and poly[1-(trimethylsilyl)-1-propyne] (PTMSP)

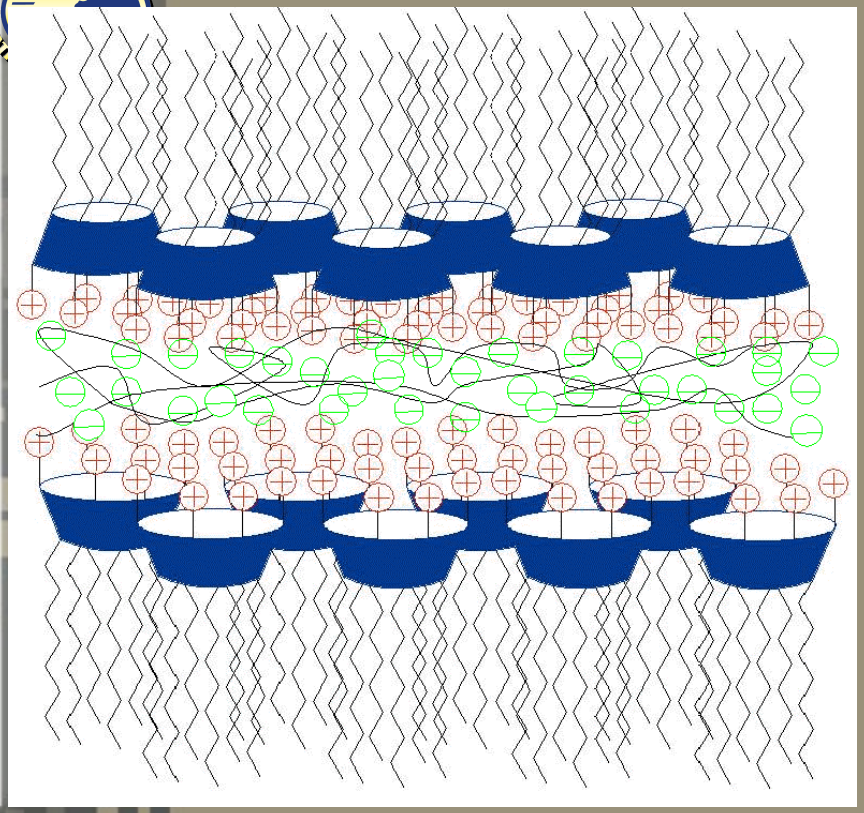


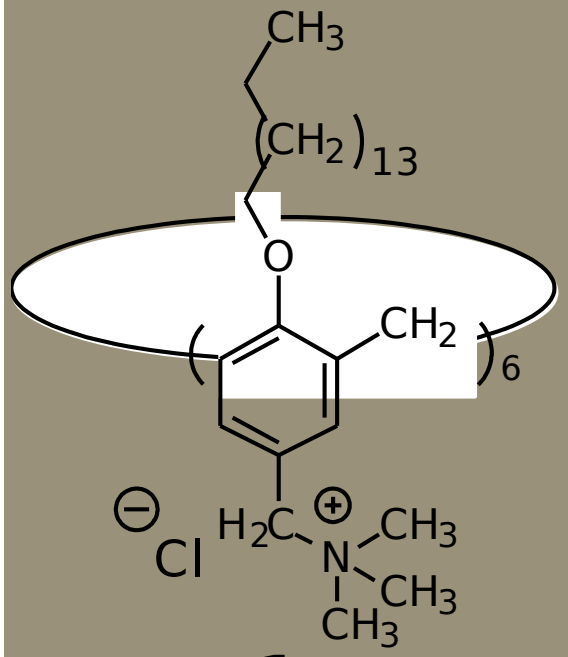
# Perforated Monolayer of II



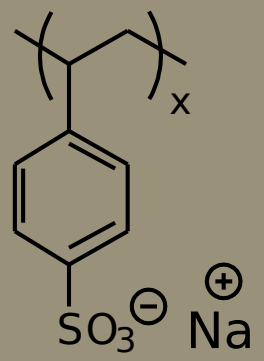
$\alpha_{He/N2} = 18$

# Glued LB Bilayer





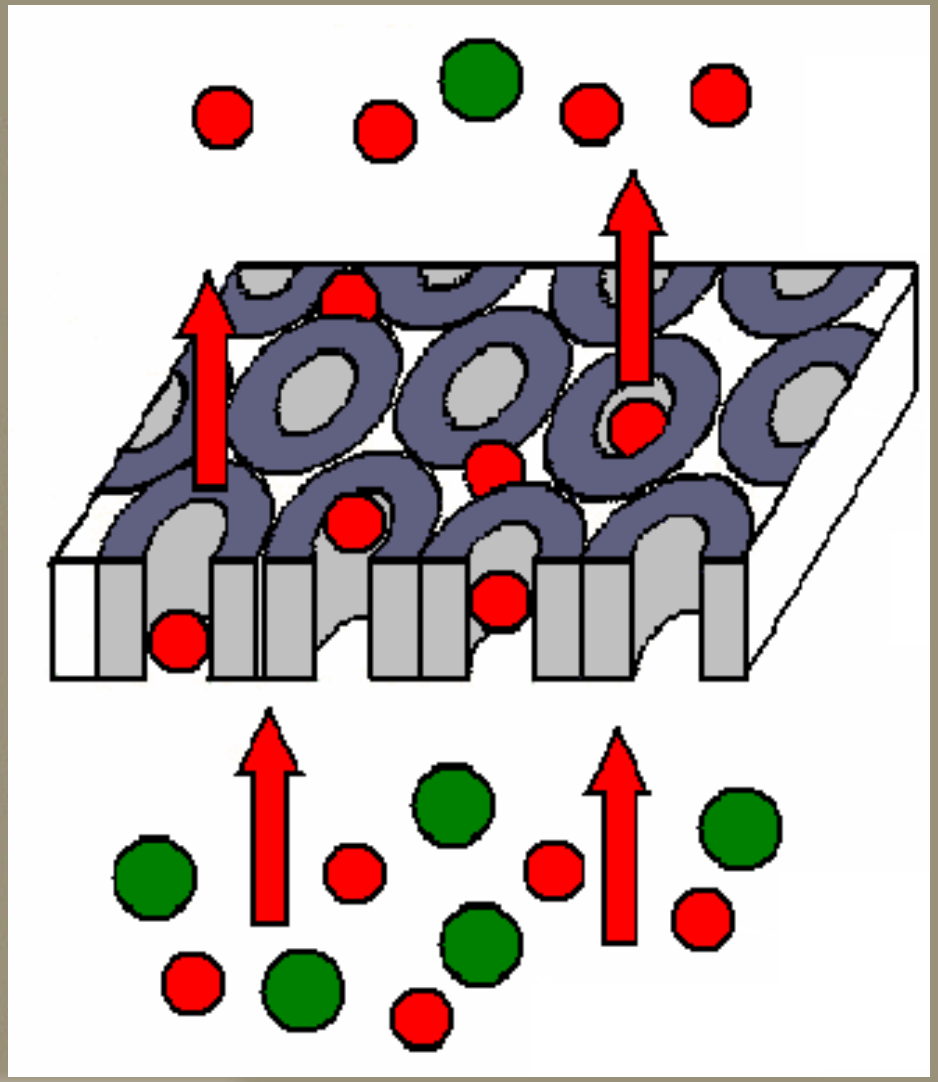

**1**




**PSS**

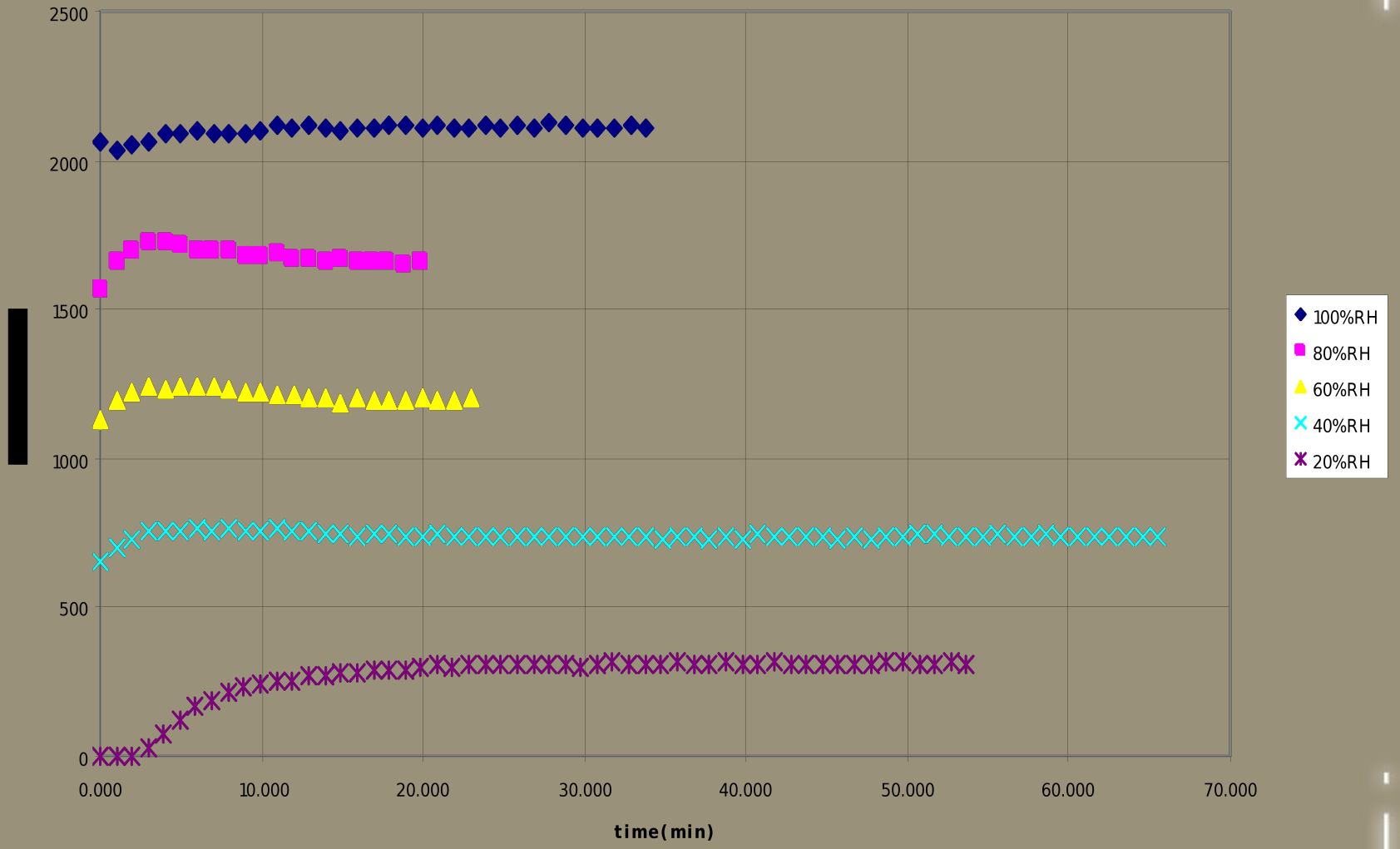
An illustration of a LB bilayer, made from a multiply charged calix[6]arene that has been glued together through the use of a polymeric counterion.

# Perforated Monolayer of III & PSS

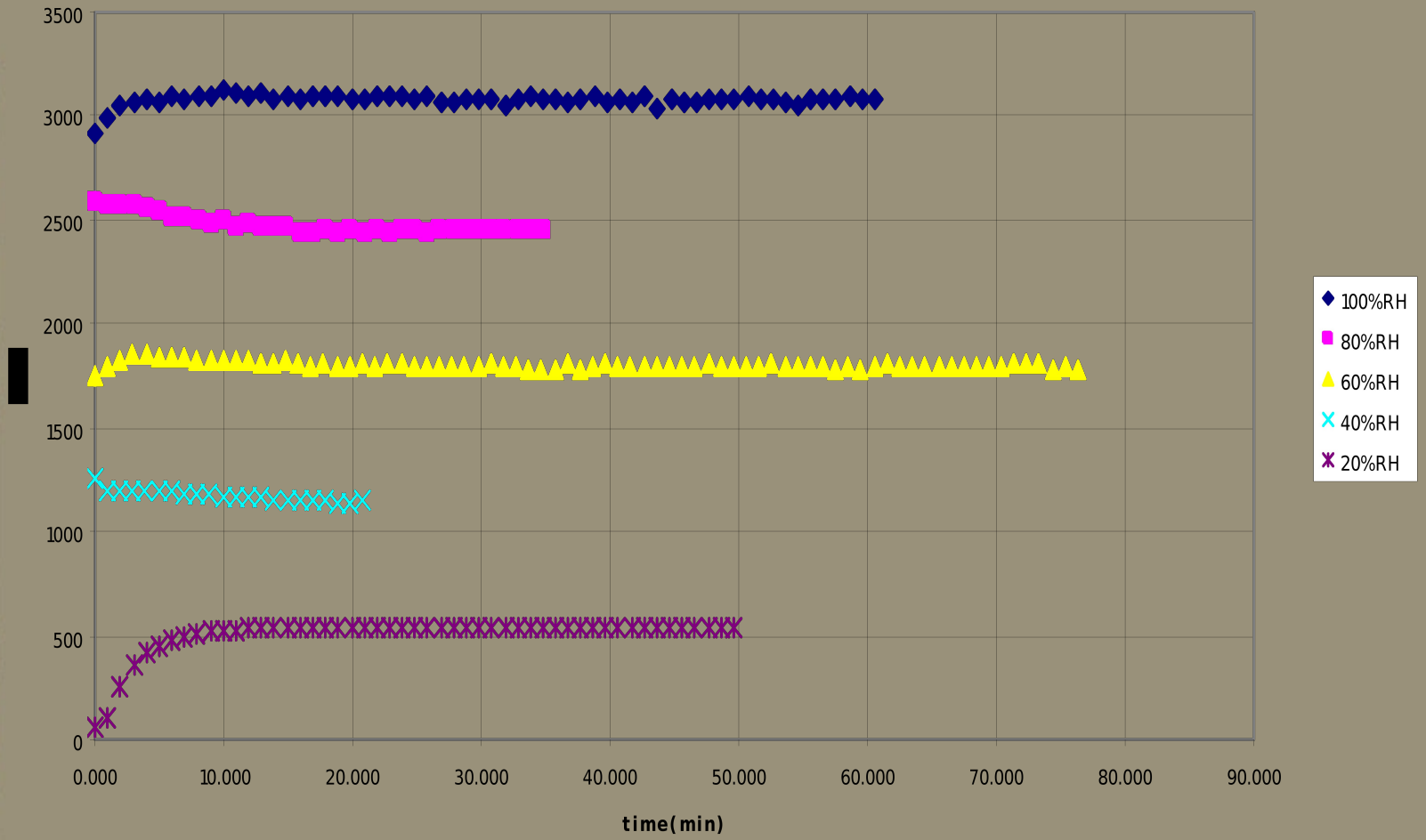


$\alpha_{He/N2} = 240$

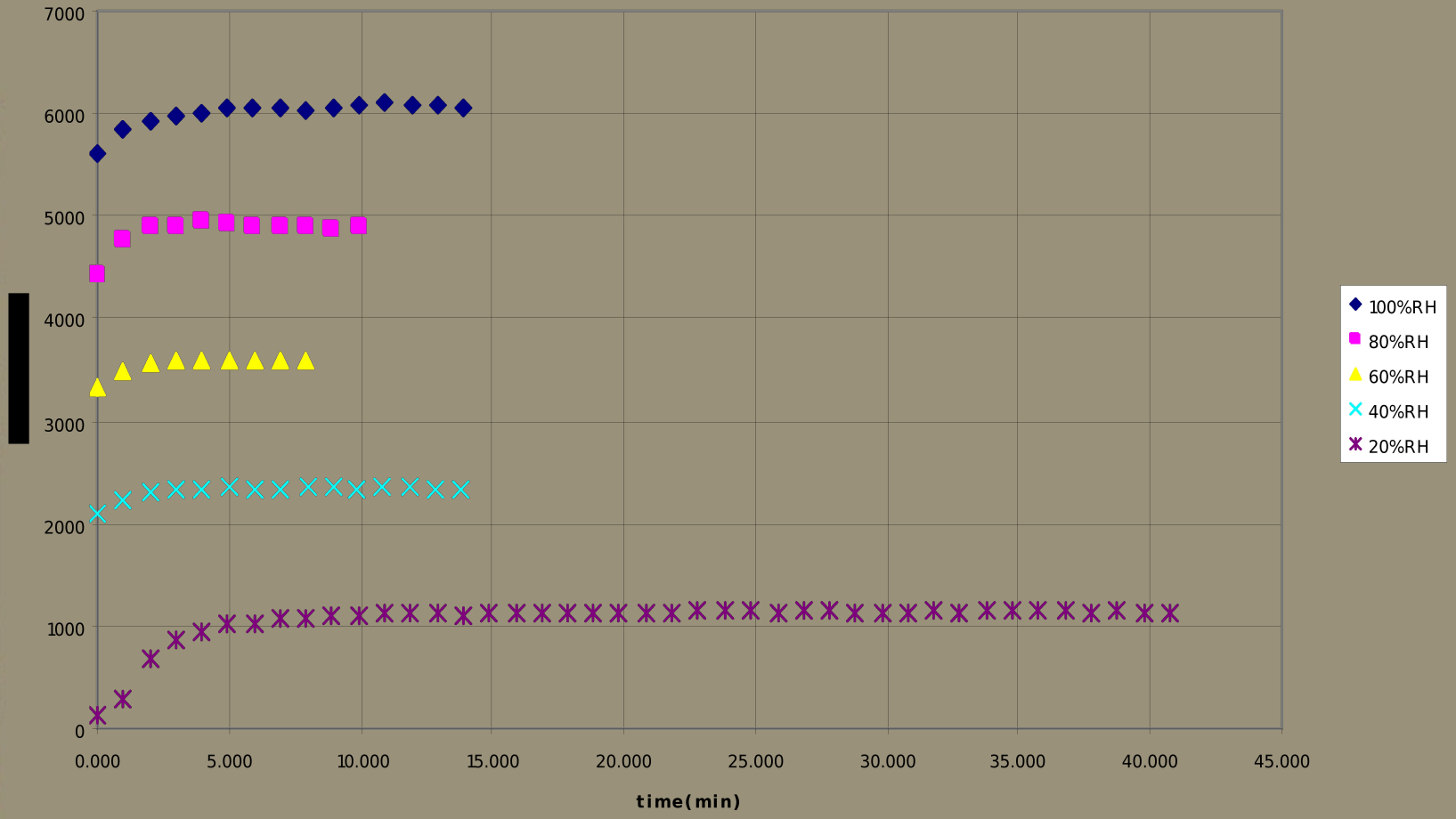
# PDMS/PS WZ04013ABCDE



# PTMSP WZ04023ABCDE



# Microporous PTFE



# Summary

- The surface modification of organic polymers by a tightly packed monolayer of calix[6]arenes or other surfactants could constitute an attractive, selectively permeable barrier, allowing the passage of water vapor (perspiration), while serving as a barrier to chemical warfare agents
- Due to its ultrathin and microporous structure, it is expected that the flux of water across such a membrane would be maximized
- The composite membranes could be used in the protective layer of the next generation of chemical protective clothing
- These novel clothing ensembles would potentially be dramatically lighter weight than current systems

# ACKNOWLEDGEMENTS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